DESCRIPTION

Vapor Grown Carbon Fiber, and Production Method and Use
Thereof

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CROSS REFERENCE TO THE RELATED APPLICATIONS

　　　This is an application based on the prescription of 35
U.S.C. Section 111(a) with claiming the benefit of filing
date of U.S. Provisional Application Serial No. 60/426,400
10　filed November 15, 2002 under the provision of 35
U.S.C.111(b), pursuant to 35 U.S.C. Section 119(e)(1).

TECHNICAL FIELD

　　　The present invention relates to a method for producing
15　carbon fiber through a vapor phase process. More
particularly, the present invention relates to a method for
producing carbon fiber having a large number of branches by
thermally.decomposing an organic compound through a vapor
phase process, to carbon fiber produced through the method,
20　and to a composite material containing the carbon fiber.

BACKGROUND ART

　　　In general, carbon fiber is dispersed in a matrix such
as resin, to thereby impart electrical conductivity and
25　thermal conductivity thereto. Vapor grown carbon fiber
(hereinafter may be abbreviated as "VGCF") is very useful,
since, even when a small amount of the carbon fiber is added

to a resin, the resultant resin composition exhibits greatly

enhanced electrical conductivity and thermal conductivity,

and therefore workability of the resin composition is not

lowered, and the surface appearance of a molded product

5   formed from the composition is not impaired (U.S. Patent

5,643,990). As has been known, when carbon fiber having a

large number of branches is added to a material, the

electrical conductivity of the material is enhanced (WO

02/049412). Therefore, demand has arisen for production of

10   carbon fiber having a large number of branches.

As one method for producing carbon fiber through a

vapor phase process, a gasification method has been proposed

(U.S. Patent 4,572,813). In the gasification method, a

solution of an organic substance in which an organo-

15   transition metallic compound is dissolved is gasified, to

thereby allow reaction to proceed at high temperature within

a heating zone. This gasification method produces carbon

fiber having a small number of branches. Meanwhile, there

has been proposed a method for producing branched carbon

20   fiber by spraying droplets of a raw material onto the wall of

a reaction tube (Japanese Patent No. 2778434). In this

method, droplets of a raw material are fed to the reaction

tube wall, to thereby grow carbon fiber on the reaction tube

wall. After the reaction tube wall is covered with the thus-

25   grown carbon fiber, droplets of the raw material are sprayed

onto the carbon fiber, a catalyst is generated on the carbon

fiber, and, on the carbon fiber serving as a substrate, fresh

carbon fiber is grown to thereby form branches, whereby branched carbon fiber is produced at high yield.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide carbon fiber having a considerably large number of branches as compared with conventional vapor grown carbon fiber through a producing method wherein the number of catalyst particles that are effectively utilized for carbon fiber growth is increased.

The present inventors have performed extensive studies on, for example, the method of feeding a raw material solution to a reaction zone of a vapor grown carbon fiber production apparatus (reaction tube), and as a result have found that carbon fiber having a large number of branches and a low bulk density is obtainable when the raw material is efficiently fed to a reaction zone maintained at a high temperature. The present invention has been accomplished on the basis of this finding.

Accordingly, the present invention provides a vapor grown carbon fiber, a method for producing the carbon fiber, and a composite material containing the carbon fiber, which are described below.

1. A vapor grown carbon fiber, each fiber filament of the carbon fiber having a branching degree of at least 0.15 occurrences/μm.

2. A vapor grown carbon fiber characterized by comprising

carbon fiber filaments, each having a branching degree of at least 0.15 occurrences/μm, in an amount of at least 10 mass%.

3. A vapor grown carbon fiber having a bulk density of 0.025 g/cm^3 or less.

4. The vapor grown carbon fiber according to 1 or 2 above, which has a bulk density of 0.025 g/cm^3 or less.

5. The vapor grown carbon fiber according to any of 1 to 3 above, which, when compressed so as to have a bulk density of 0.8 g/cm^3, has a specific resistance of 0.025 Ωcm or less.

6. The vapor grown carbon fiber according to any of 1 to 3 above, each fiber filament of the carbon fiber having a diameter of 1 to 500 nm.

7. The vapor grown carbon fiber according to any of 1 to 3 above, which is produced by feeding a raw material solution containing a carbon source and a transition metallic compound into a reaction zone through spraying at a spray angle of 3° to 30° and subjecting the raw material solution to thermal decomposition.

8. The vapor grown carbon fiber according to any of 1 to 6 above, which is produced by feeding a raw material solution containing a carbon source and a transition metallic compound into a reaction zone through spraying, while feeding a carrier gas through at least one site other than an inlet through which the raw material solution is sprayed, and subjecting the raw material solution to thermal decomposition.

9. A method for producing a vapor grown carbon fiber comprising spraying a raw material solution containing a

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carbon source and a transition metallic compound into a

reaction zone and subjecting the raw material solution to

thermal decomposition, characterized in that the raw material

solution is sprayed at a spray angle of 3° to 30°.

5   10. The method for producing a vapor grown carbon fiber

according to 9 above, wherein droplets of the raw material

solution have an average diameter of at least 5 μm.

11. The method for producing a vapor grown carbon fiber

according to 9 or 10 above, wherein the raw material solution

10   and a carrier gas are fed through a concentric multi-tube

nozzle into a reaction tube.

12. The method for producing a vapor grown carbon fiber

according to 11 above, wherein the raw material solution is

fed through one of the tubes of the multi-tube nozzle, and

15   another tube serves as a passage for the carrier gas only.

13. The method for producing a vapor grown carbon fiber

according to 12 above, wherein the raw material solution and

the carrier gas are fed through the inner tube of

concentrically disposed two tubes, and the carrier gas is fed

20   through the outer tube of the tubes.

14. The method for producing a vapor grown carbon fiber

according to 12 above, wherein the carrier gas is fed through

the innermost tube and the outermost tube of concentrically

disposed three tubes, and the middle tube of the tubes serves

25   as a passage for the raw material solution only.

15. A method for producing a vapor grown carbon fiber

comprising spraying a raw material solution containing a

carbon source and a transition metallic compound into a

reaction zone and subjecting the raw material solution to

thermal decomposition, characterized in that a carrier gas is

fed through at least one site other than an inlet through

5   which the raw material solution is sprayed.

16. The method for producing a vapor grown carbon fiber

according to 15 above, wherein the raw material solution is

sprayed at a spray angle of 3° to 30°.

17. The method for producing a vapor grown carbon fiber

10   according to 9 or 15 above, wherein the raw material solution

containing a carbon source and a transition metallic compound

further contains a surfactant and/or thickening agent.

18. The method for producing a vapor grown carbon fiber

according to 9 or 15 above, which comprises heating and

15   firing recovered carbon fiber in a non-oxidative atmosphere

at 800°C to 1,500°C and subsequently heating the thus-fired

carbon fiber in a non-oxidative atmosphere at 2,000 to

3,000°C, to thereby graphitize the carbon fiber.

19. The method for producing a vapor grown carbon fiber

20   according to 18 above, wherein, before being graphitized

through heating, the recovered carbon fiber is doped with at

least one boron compound, serving as a crystallization

facilitating compound, selected from the group consisting of

boron, boron oxide, boron carbide, a boric ester, boric acid

25   or a salt thereof, and an organic boron compound in an amount

of 0.1 to 5 mass% as reduced to boron.

20. A composite material comprising a vapor grown carbon

                                    6

fiber according to any of 1 to 8 above.

21. A composite material comprising a vapor grown carbon

fiber produced through a method according to any of 9 to 19

above.

5   22. A resin composition comprising a vapor grown carbon

fiber according to any of 1 to 8 above.

23. A resin composition comprising a vapor grown carbon

fiber produced through a method according to any of 9 to 19

above.

10   Main raw materials (essential raw materials) employed

for producing the carbon fiber of the present invention are

an organic compound and a transition metallic compound.

No particular limitations are imposed on the organic

compound which may be employed as a raw material of the

15   carbon fiber, so long as the organic compound assumes to be

in a liquid form. Specific examples of the organic compound

which may be employed include aromatic compounds such as

benzene, toluene and xylene; linear-chain hydrocarbons such

as hexane and heptane; cyclic hydrocarbons such as

20   cyclohexane; alcohols such as methanol and ethanol; gasoline;

and kerosene. Aromatic compounds are preferred, with benzene

being most preferred. These carbon sources may be employed

singly or in combination of two or more species. In the case

of feeding of an organic compound, the entirety of the

25   compound may be fed in the form of droplets. Alternatively,

a portion of the organic compound may be fed in the form of

droplets, and the remaining portion of the compound may be

fed in the form of liquid or gas.

The transition metallic compound serving as a catalyst
is preferably an organic or inorganic compound containing a
metal belonging to Group IVa, Va, VIa, VIIa or VIII.

5   Particularly, Fe compounds, Ni compounds and Co compounds
(e.g., ferrocene and nickelocene), which are transition
metallic compounds that generate transition metal ultrafine
seeds, are preferred.

Productivity of the carbon fiber can be enhanced by

10 adding a sulfur source serving as a promoter to the raw
material solution. The sulfur source may be elemental sulfur,
an organic sulfur compound such as thiophene or an inorganic
sulfur compound such as hydrogen sulfide. However, from the
viewpoint of handling, elemental sulfur and thiophene, which

15 are dissolved in a carbon source, are preferred. These
sulfur sources (elemental sulfur and sulfur compounds) may be
employed singly or in combination of two or more species.

The raw material solution is prepared by dissolving a
transition metallic compound in an organic compound.

20 Droplets of the raw material solution are preferably
generated through the spraying method shown in Fig. 3, which
employs a spray nozzle.

Preferably, the raw material droplets are heated as
quickly as possible to the temperature of a reaction zone of

25 a reactor, the temperature being determined to be equal to or
higher than the decomposition temperature of the organic
compound. This is because the decomposition temperature of

the transition metallic compound is generally lower than that
of the organic compound, and therefore, when the raw material
droplets are heated slowly, the transition metallic compound
decomposes to thereby generate fine particles of the metal

5   before growth of carbon fiber, and the resultant fine
particles collide with one another and are grown into large
particles until they no longer exhibit a catalyst function.
Quick feeding of the raw material droplets to the high-
temperature zone by use of a spray nozzle is effective for

10 generating large amounts of catalyst particles which can be
employed for growth of carbon fiber. During the course of
feeding of the droplets, a critical point is to regulate the
spray angle of the raw material solution or the diameter of
each of the droplets by varying, for example, the shape of

15 the spray nozzle and the viscosity, surface tension and
density of the raw material solution.

   Specifically, the spray angle of the raw material
solution is preferably 3° to 30°, more preferably 5° to 25°.
As used herein, the term "spray angle" refers to, as shown in

20 Fig. 1, an angle θ (vertical angle) formed by the outermost
trajectories of the raw material droplets with the tip
portion of a nozzle serving as the vertex. When the spray
angle exceeds 30°, the droplets tend to collide against a
reaction wall section whose temperature is low, the

25 temperature increasing rate of the droplets which do not
reach a high-temperature section becomes low, and the amount
of effective catalyst particles decreases, whereby the

resultant carbon fiber comes to have a small number of branches. In contrast, when the spray angle is less than 3°, the amount of the droplets which pass through the high-temperature section increases, and the conversion rate of the

5   raw material is lowered, leading to low yield of the carbon fiber.

Each of the raw material droplets preferably has a diameter of 5 μm or more, more preferably 5 to 300 μm, much more preferably 10 to 100 μm. When the raw material droplet

10 has a diameter of less than 5 μm, the gasification rate of the droplets increases and the droplets do not reach the high-temperature section. As a result, the temperature increasing rate of the droplets is lowered and the number of effective catalyst particles decreases, whereby the resultant

15 carbon fiber comes to have a small number of branches. In contrast, when the raw material droplet has a diameter exceeding 300 μm, heating the raw material requires a long period of time, and thus the conversion rate of the raw material is lowered. As used herein, the droplet diameter is

20 measured by means of the Doppler method as follows. Specifically, the raw material solution is sprayed outside a reaction tube by causing air to flow through a spray nozzle; the thus-sprayed droplet particles are irradiated with two crossed laser beams; light scattered by the particles that

25 have passed through interference fringes is detected by a light-receiving device provided at a certain location; and the diameters of the particles are calculated on the basis of

the phase difference. The average of the thus-calculated

diameters of the particles is taken as the droplet diameter.

No particular limitations are imposed on the shape of

the nozzle, so long as the droplet diameter and the spray

5   angle fall within predetermined ranges. Preferably, the

nozzle has a structure such that the droplet diameter and the

spray angle can be readily regulated.

Specifically, there may be employed a nozzle having,

for example, a concentric multi-tube structure, a single-

10   fluid-type structure or a double-fluid-type structure (an

interior mixing type in which a reactant solution and a

carrier gas are mixed in the interior of a nozzle, or an

exterior mixing type in which a reactant solution and a

carrier gas are mixed outside a nozzle). Particularly, a

15   nozzle having a concentric multi-tube structure or a double-

fluid-type structure is preferred. When a double-fluid-type

nozzle is employed, the droplet diameter can be regulated by

varying the feed amount of the raw material solution or a

carrier gas, and the spray angle can be regulated by varying

20   the structure of the nozzle.

Specific examples of the nozzle of concentric multi-

tube structure which may be employed include a nozzle of

double-tube structure (its vertical cross-sectional view is

shown in Fig. 2(A)) and a nozzle of triple-tube structure

25   (its vertical cross-sectional view is shown in Fig. 2(B)).

In order to regulate the spray angle of the raw material

solution, preferably, at least a portion of a carrier gas (3)

to be fed to a reaction tube (1) is fed through a tube other
than a tube through which the raw material solution (4) is
fed. In the case where a nozzle of double-tube structure is
employed, when the raw material solution (4) and a carrier

5   gas (hydrogen) (3) are fed through the inner tube (5), a
portion of the carrier gas (3) is fed through the outer tube
(6), and the spray angle can be readily regulated by
increasing the amount of hydrogen (3) fed through the outer
tube (6). At the spraying side (8) in a nozzle of double-

10. tube structure, the inner tube may be longer or shorter than
the outer tube. Employing the inner tube longer than the
outer tube is preferable, as the spray angle is readily
regulated. In the case of a nozzle of double-tube structure
(2), the diameter of the inner tube is preferably 0.01 to 2

15   mm, more preferably 0.1 to 0.5 mm, and the clearance between
the outer tube and the inner tube (d) is preferably 0.01 to 2
mm, more preferably 0.1 to 0.5 mm. When the diameter of the
inner tube and the clearance between the outer tube and the
inner tube exceed 2 mm, the raw material solution fails to be

20   sprayed normally, and carbon fiber may fail to be generated
as a result of growth of catalyst particles, whereas when the
diameter of the inner tube and the clearance between the
outer tube and the inner tube are less than 0.01 mm, the feed
amounts of the raw material and the carrier gas fail to be

25   increased, and thus productivity of carbon fiber is lowered.

In the case where a nozzle of triple-tube structure is
employed, a carrier gas (3) is fed through the innermost tube

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(5) and the outermost tube (6), and the raw material solution
is fed through the middle tube (7). In this case, when the
rate of the carrier gas fed through the innermost and
outermost tubes is regulated, the spray angle of the raw

5   material solution can be readily regulated so as to fall
within a range of 3° to 30°. At the spraying side (8) in a
nozzle of triple-tube structure, the length of the innermost,
middle and outermost tubes may be different. Employing the
middle tube longer than the outermost tube is preferable, as

10   the spray angle is readily regulated. As in the case of a
nozzle of double-tube structure, the diameter of the
innermost tube (5), the clearance between the outermost tube
(6) and the middle tube (7), and the clearance between the
middle tube and the innermost tube are preferably 0.01 to 2

15   mm, more preferably 0.1 to 0.5 mm.

    Generally, the droplet diameter varies depending on the
viscosity, surface tension and density of the solution to be
sprayed. The droplet diameter can be regulated to a
desirable size by adding a thickening agent, surfactant, etc.

20   to the raw material solution.

    Generally, the droplet diameter becomes larger when the
viscosity of the raw material solution increases. Therefore,
adding a thickening agent to the raw material solution
enables to feed the raw material droplets to the high-

25   temperature zone. There is no particular limitation on a
thickening agent as long as it has a higher viscosity than
that of the organic compound of the raw material and can be

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dissolved in the raw-material organic compound. Specifically, mineral oil, vegetable oil, vegetable fat, paraffin, fatty acids (oleic acid, linolic acid, etc.), fatty alcohol (decanol, octanol, etc.), polymer (polyvinylalcohol,

5   polyethyleneglycol, polypropyleneglycol, etc.) are used.

As a surfactant, cation surfactant, anion surfactant, nonionic surfactant and ampholytic surfactant can be used. Desirable surfactants include $C_nH_{2n+1}SO_3M$ (n = 8 to 16, M = Na, K, Li, $N(CH_3)_4$), $C_nH_{2n+1}SO_4M$ (n = 8 to 16, M = Na, K, Li,

10   $N(CH_3)_4$), $(C_nH_{2n+1})_2COOCH_2COOCHSO_3M$ (n = 8 to 16, M = Na, K, Li, $N(CH_3)_4$), $C_nH_{2n+1}N(CH_3)_3X$ (n = 8 to 15, X = Br, Cl, I), $C_nH_{2n+1}N(CH_3)_2CH_2COO$ (n = 8 to 15), $C_nH_{2n+1}CHOHCH_2OH$ (n = 8 to 15) and $C_nH_{2n+1}(OC_2H_4)_mHCH_2OH$ (n = 8 to 15, m =3 to 8).

In order to feed the raw material and a transition

15   metallic compound serving as a catalyst to a thermal decomposition zone for developing and maintaining the activity of the catalyst, a carrier gas containing at least a reducing gas such as hydrogen gas is employed. The amount of the carrier gas is appropriately 1 to 100 parts by mol on the

20   basis of 1.0 part by mol of an organic compound serving as a carbon source.

No particular limitations are imposed on the location at which the carrier gas is brought into the reaction tube. As shown in Fig. 3, when hydrogen gas is fed through at least

25   one inlet (preferably four inlets) other than the inlet through which the raw material solution is fed, the gas in the reaction tube develops turbulence and transfer of heat

from the reaction tube wall is promoted, leading to an increase in yield of carbon fiber.

A vertical electric furnace is generally employed as a reaction furnace. The temperature of the reaction furnace is 5   800 to 1,300°C, preferably 1,000 to 1,300°C. The raw material solution and a carrier gas are fed to the reaction furnace heated to a predetermined temperature so as to allow reaction to proceed, thereby producing carbon fiber.

The thus-produced carbon fiber is preferably subjected 10   to heat treatment for removal of volatile components and for graphitization of the carbon fiber. Removal of volatile components is carried out by recovering the carbon fiber containing branched carbon fiber filaments produced in the reaction furnace and then heating and firing the carbon fiber 15   at 800°C to 1,500°C in a non-oxidative atmosphere such as argon gas. Subsequently, the thus-treated carbon fiber is further heated at 2,000 to 3,000°C in a non-oxidative atmosphere to thereby allow graphitization to proceed. During the course of graphitization, the carbon fiber is 20   doped with a small amount of a crystallization facilitating element to thereby enhance crystallinity of the fiber. The crystallization facilitating element is preferably boron. Since the surface of the thus-graphitized fine carbon fiber is covered with a dense basal plane (a plane of hexagonal 25   network structure), preferably, carbon fiber of low crystallinity which has been heated at 1,500°C or lower is doped with boron. Even when carbon fiber of low

crystallinity is employed, carbon fiber of high crystallinity
can be obtained since the carbon fiber is heated to its
graphitization temperature when being doped with boron; i.e.,
when being subjected to boronization.

5   The doping amount of boron is generally 5 mass% or less
on the basis of the entire amount of carbon. When carbon
fiber is doped with boron in an amount of 0.1 to 5 mass%, the
crystallinity of the carbon fiber can be effectively enhanced.
Therefore, elemental boron or a boron compound (e.g., boron

10   oxide (B_2O_3), boron carbide (B_4C), a boric ester, boric acid
(H_3BO_3) or a salt thereof or an organic boron compound),
which serves as a crystallization facilitating compound, is
added to carbon fiber such that the boron content of the
carbon fiber falls within the above range. In consideration

15   of the conversion rate, the amount of the boron compound as
reduced to boron is 0.1 to 5 mass% on the basis of the entire
amount of carbon. It should be noted that the key
requirement is that boron be present when the fiber is
crystallized through heat treatment. Boron may be evaporated

20   during the course of, for example, high-temperature treatment
performed after carbon fiber has been highly crystallized,
and thus the boron content of the carbon fiber may become
lower than the amount of boron initially added to the fiber.
Such a drop is acceptable so long as the amount of boron (B)

25   remaining in the thus-treated carbon fiber is about 0.01
mass% or more.

       The temperature required for introducing boron into

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carbon crystals or the surface of carbon fiber is 2,000°C or

higher, preferably 2,300°C or higher. When the heating

temperature is lower than 2,000°C, introduction of boron

becomes difficult because of low reactivity between boron and

5   carbon. Heat treatment is carried out in a non-oxidative

atmosphere, preferably in an atmosphere of a rare gas such as

argon. When heat treatment is carried out for an excessively

long period of time, sintering of carbon fiber proceeds,

resulting in low yield. Therefore, after the temperature of

10   the center portion of carbon fiber reaches the target

temperature, the carbon fiber is maintained at the target

temperature within one hour.

        The carbon fiber produced through the method of the

present invention has a large number of branches and thus

15   readily forms a strong fiber network. Therefore, even when a

small amount of the carbon fiber is added to a matrix such as

resin, the electrical conductivity and thermal conductivity

of the matrix are enhanced. When the carbon fiber produced

through the method of the present invention is compressed

20   into a compact, the carbon fiber compact exhibits low

specific resistance, since a strong fiber network is formed.

The carbon fiber produced through the method of the present

invention has a low bulk density, and filaments of the fiber

are not strongly entangled with one another. Therefore, the

25   carbon fiber is characterized in exhibiting a good dispersity

when mixed in a material such as resin.

        In the present invention, the diameter and branching

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degree of each fiber filament of the carbon fiber are
obtained through observation of the filament under an
electron microscope. The branching degree (b/ΣL) is
calculated from the sum of the lengths (ΣL) of the carbon

5   fiber filaments and the total branching points (b) of the
filaments, both being measured within a field of view. That
is, the branching degree is defined by the number of
branching points per unit filament length. A characteristic
feature of the carbon fiber of the present invention resides

10   in that each fiber filament of the fiber has a branching
degree of 0.15 occurrences/μm or more. Preferably, a
branching degree is between 0.15 occurrences/μm and 10
occurrences/μm and more preferably between 0.15
occurrences/μm and 1 occurrences/μm. In the case where the

15   branching degree is less than 0.15 occurrences/μm, when a
small amount (about 1 mass%) of the carbon fiber is added to
a material, the electrical conductivity of the material is
barely enhanced. From the viewpoint of enhancement of
electrical conductivity, preferably, the carbon fiber

20   contains carbon fiber filaments having such a branching
degree in an amount of 10 mass% or more.

The conventional gasification method produces carbon
fiber containing substantially no branching portions, and
conventional vapor grown carbon fiber (VGCF) has a branching

25   degree of less than 0.15 occurrences/μm. When a small amount
of such carbon fiber is added to a material, the electrical
conductivity of the material is barely enhanced.

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Another characteristic feature of the carbon fiber of
the present invention resides in that the carbon fiber has a
bulk density of 0.025 g/cm^3 or less. Preferably, the bulk
density is between 0.01 g/cm^3 and 0.025 g/cm^3. In order to
5   enhance reproducibility of measurement, the bulk density of
the carbon fiber is obtained through the following procedure:
the produced carbon fiber is heated in an argon atmosphere at
1,000°C for 15 minutes and then vibrated by use of a
vibration apparatus for one minute to thereby prepare a
10   measurement sample; the sample (1 g) is placed into a 100-ml
messcylinder and a microspatula is inserted thereinto, and
the sample is stirred through vibration by use of a test tube
Touch mixer for one minute; the resultant sample is stirred
manually 10 times, and the microspatula is removed from the
15   messcylinder, followed by vibration of the messcylinder by
use of the Touch mixer for one minute; and the volume of the
sample is measured and the bulk density is calculated from
the mass and the volume of the sample.

Carbon fiber produced through the conventional
20   gasification method has a bulk density of about 0.03 g/cm^3,
and conventional vapor grown carbon fiber (VGCF) has a bulk
density of about 0.04 g/cm^3. When a small amount of such
carbon fiber is added to a material, the electrical
conductivity of the material is barely enhanced.

25   Since the carbon fiber of the present invention is in a
fibrous form, the carbon fiber is compressed into a compact
having a bulk density of 0.8 g/cm^3, and the compact is

subjected to measurement of specific resistance to determine

the specific resistance of the carbon fiber. The specific

resistance of the carbon fiber is preferably 0.025 Ωcm or

less. In the case where the specific resistance is above

5   0.025 Ωcm, the electrical conductivity of the material is

barely enhanced when a small amount (about 1 mass%) of the

carbon fiber is added to a material.

No particular limitations are imposed on the diameter

of each fiber filament of the carbon fiber, but the diameter

10   is preferably 1-500 nm or thereabouts, more preferably 5 to

200 nm, from the viewpoint of enhancement of electrical

conductivity.

The carbon fiber produced through the method of the

present invention has a high branching degree, and thus

15   exhibits excellent characteristics such as high electrical

conductivity and high thermal conductivity. Therefore, when

the carbon fiber is mixed with a matrix such as resin, metal

or ceramic to thereby prepare a composite material, the

matrix exhibits, for example, enhanced electrical

20   conductivity and thermal conductivity.

Examples of the resin which may be employed in the

composite material include thermoplastic resins and

thermosetting resins. Specific examples include polyethylene

(PE), polypropylene, nylon, urethane, polyacetal,

25   polyphenylene sulfide, polystyrene, polycarbonate,

polyphenylene ether, polyethylene terephthalate, polybutylene

terephthalate, polyarylate, polysulfone, polyethersulfone,

polyimide, polyoxybenzoyl, polyether ether ketone,

polyetherimide, Teflon (registered trademark), silicon resin,

cellulose acetate resin, ABS resin, AES resin, ABMS resin,

AAS resin, phenol resin, urea resin, melamine resin, xylene

5   resin, diallyl phthalate resin, epoxy resin, aniline resin

and furan resin.

Examples of the ceramic matrix include aluminum oxide,

mullite, silicon oxide, zirconium oxide, silicon carbide and

silicon nitride.

10   Examples of the metal matrix include gold, silver,

aluminum, iron, magnesium, lead, copper, tungsten, titanium,

niobium, hafnium, alloys thereof and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

15   Fig. 1 is an explanatory view of the spray angle of a

raw material solution.

Fig. 2(A) and 2(B) are vertical cross-sectional views

showing the structures of a double-tube raw material feed

nozzle and a triple-tube raw material feed nozzle,

20   respectively, employed in the method of the present invention.

Fig. 3 shows an example of bringing a hydrogen carrier

gas into a reaction tube through a site other than an inlet

through which a raw material solution is sprayed.

Fig. 4 is a schematic cross-sectional view showing a

25   vapor grown carbon fiber production system employed in

Comparative Example 1.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will next be described with reference to Examples and Comparative Examples, but the present invention is not limited to the below-described

5   Examples.

Example 1:

Ferrocene (0.83 kg) and sulfur (0.059 kg) were dissolved in benzene (14 kg) to thereby prepare a raw

10   material solution (ferrocene content of the solution: 5.5 mass%, sulfur content of the solution: 0.39 mass%). Nitrogen gas was caused to flow through a reaction furnace system (1) shown in Fig. 3, which includes a vertical heating furnace (1)(inner diameter: 370 mm, length: 2,000 mm) whose top

15   portion is equipped with a raw material feed nozzle (spray nozzle)(2)(SU11, product of Spraying Systems Co.), to thereby purge oxygen gas from the furnace system. Subsequently, hydrogen gas was caused to flow through the furnace system to thereby fill the furnace system with hydrogen gas.

20   Thereafter, the temperature of the reaction furnace was raised to 1,250°C. By use of a pump, the raw material solution (130 g/min) and hydrogen gas (20 L/min) were fed through the raw material feed nozzle, and hydrogen gas (400 L/min) was fed through a flange (9) provided on the upper

25   portion of the reaction furnace. The spray angle of the raw material solution and the average diameter of the sprayed droplets were 21° and 30 μm, respectively. Under the above

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conditions, reaction was allowed to proceed for one hour to thereby produce carbon fiber. The resultant carbon fiber was found to have a bulk density of 0.021 g/cm^3. The carbon fiber was found to have a specific resistance of 0.0236 Ωcm

5   when being compressed so as to have a bulk density of 0.8 g/cm^3.

The thus-produced carbon fiber was observed under an electron microscope, and the average diameter of fiber filaments of the carbon fiber was found to be about 80 nm.

10   The branching degree of each fiber filament was measured, and found to be 0.3 occurrences/μm. The mass of the carbon fiber was measured and carbonization yield (the mass of the produced carbon fiber/the mass of the fed benzene) was calculated to be 55%.

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Example 2:

The vapor grown carbon fiber produced in Example 1 was fired at 1,000°C for 15 minutes and then graphitized at 2,800°C for 15 minutes. The thus-graphitized carbon fiber

20   was dispersed in polyacetal by use of a kneader to thereby prepare a compound. The vapor grown carbon fiber was added to the resin in an amount of 5 mass%. The resultant compound was molded into a product by use of a thermal press and the volume resistivity of the molded product was measured by

25   means of the four-terminal method. The volume resistivity was found to be 300 Ωm.

Example 3:

Nitrogen gas was caused to flow through a reaction furnace system (1) shown in Fig. 3, which includes a vertical heating furnace (inner diameter: 370 mm, length: 2,000 mm)

5   whose top portion is equipped with a double-tube raw material feed nozzle having a structure shown in Fig. 2(A), to thereby purge oxygen gas from the furnace system. Subsequently, hydrogen gas was caused to flow through the furnace system to thereby fill the furnace system with hydrogen gas.

10   Thereafter, the temperature of the reaction furnace was raised to 1,250°C.

By use of a pump, a raw material solution (a benzene solution containing ferrocene in an amount of 4.5 mass% and sulfur in an amount of 0.32 mass%) (50 g/min) and hydrogen

15   gas (5 L/min) were fed through the inner tube (5) of the raw material feed nozzle, hydrogen gas (10 L/min) was fed through the outer tube (6) of the nozzle, and hydrogen gas (200 L/min) was fed through a flange (9) provided on the upper portion of the reaction furnace. The spray angle of the raw

20   material solution and the average diameter of the sprayed droplets were 26° and 30 μm, respectively. Under the above conditions, reaction was allowed to proceed for one hour to thereby produce carbon fiber. The resultant carbon fiber was found to have a bulk density of 0.022 g/cm^3. The carbon

25   fiber was found to have a specific resistance of 0.027 Ωcm when being compressed so as to have a bulk density of 0.8 g/cm^3. The thus-produced carbon fiber was observed under an

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electron microscope, and the average diameter of fiber

filaments of the carbon fiber was found to be about 100 nm.

The branching degree of each fiber filament was measured and

found to be 0.3 occurrences/µm. The mass of the carbon fiber

5   was measured, and carbonization yield (the mass of the carbon

fiber/the mass of the fed benzene) was calculated to be 60%.

Example 4:

Nitrogen gas was caused to flow through a reaction

10   furnace system (1) shown in Fig. 3, which includes a vertical

heating furnace (inner diameter: 130 mm, length: 2,000 mm)

whose top portion is equipped with a double-tube raw material

feed nozzle having a structure shown in Fig. 2(A), to thereby

purge oxygen gas from the furnace system. Subsequently,

15   hydrogen gas was caused to flow through the furnace system to

thereby fill the furnace system with hydrogen gas.

Thereafter, the temperature of the reaction furnace was

raised to 1,250°C.

By use of a pump, a raw material solution (a benzene

20   solution containing ferrocene in an amount of 7 mass% and

sulfur in an amount of 0.5 mass%) (18 g/min) and hydrogen gas

(5 L/min) were fed through the inner tube (5) of the raw

material feed nozzle, hydrogen gas (10 L/min) was fed through

the outer tube (6) of the nozzle, and hydrogen gas (450

25   L/min) was fed through a flange (9) provided on the upper

portion of the reaction furnace. The spray angle of the raw

material solution and the average diameter of the sprayed

droplets were 26° and 20 μm, respectively. Under the above

conditions, reaction was allowed to proceed for one hour to

thereby produce carbon fiber. The resultant carbon fiber was

found to have a bulk density of 0.049 g/cm^3. The carbon

5   fiber was found to have a specific resistance of 0.042 Ωcm

when being compressed so as to have a bulk density of 0.8

g/cm^3.

The thus-produced carbon fiber was observed under an

electron microscope, and the average diameter of fiber

10   filaments of the carbon fiber was found to be about 9 nm.

The branching degree of each fiber filament was measured and

found to be 0.2 occurrences/μm. The mass of the carbon fiber

was measured and carbonization yield (the mass of the

produced carbon fiber/the mass of the fed benzene) was

15   calculated to be 15%.

Example 5:

Ferrocene (1 kg), sulfur (0.05 kg) and

polypropyleneglycol (D-400, product of NOF Corporation,

20   molecular weight: 400, decomposition temperature: 290°C)

(0.5kg) were dissolved in benzene (13.5 kg) to thereby

prepare a raw material solution (containing ferrocene, sulfur

and polyporpyleneglycol in the amount of 7 mass%, 0.4 mass%

and 3 mass% respectively). Nitrogen gas was caused to flow

25   through a reaction furnace system (1) shown in Fig. 3, which

includes a vertical heating furnace (1)(inner diameter: 370

mm, length: 2,000 mm) whose top portion is equipped with a

raw material feed nozzle (spray nozzle)(2)(SU11, product of
Spraying Systems Co.), to thereby purge oxygen gas from the
furnace system. Subsequently, hydrogen gas was caused to
flow through the furnace system to thereby fill the furnace

5   system with hydrogen gas. Thereafter, the temperature of the
reaction furnace was raised to 1,250°C.

By use of a pump, a raw material solution (230 g/min)
and hydrogen gas (5 L/min) and hydrogen gas (20 L/min) were
fed through the raw material feed nozzle, and hydrogen gas

10   (400 L/min) was fed through a flange (9) provided on the
upper portion of the reaction furnace. The spray angle of
the raw material solution was 21° and the average diameter of
the sprayed droplets was 40 μm. Under the above conditions,
reaction was allowed to proceed for one hour to thereby

15   produce carbon fiber. The resultant carbon fiber was found
to have a bulk density of 0.024 g/cm^3. The carbon fiber was
found to have a specific resistance of 0.024 Ωcm when being
compressed so as to have a bulk density of 0.8 g/cm^3.

The thus-produced carbon fiber was observed under an

20   electron microscope, and the average diameter of fiber
filaments of the carbon fiber was found to be about 80 nm.
The branching degree of each fiber filament was measured and
found to be 0.4 occurrences/μm. The mass of the carbon fiber
was measured and carbonization yield (the mass of the carbon

25   fiber/the mass of the fed benzene) was calculated to be 57%.

Comparative Example 1:

Carbon fiber was produced by use of a system shown in

Fig. 4, which includes a vertical heating furnace (inner

diameter: 370 mm, length: 2,000 mm) whose top portion is

equipped with a double-fluid-type hollowcone raw material

5   feed nozzle. Nitrogen gas was caused to flow through the

furnace system to thereby purge oxygen gas from the furnace

system. Subsequently, hydrogen gas was caused to flow

through the furnace system to thereby fill the furnace system

with hydrogen gas. Thereafter, the temperature of the

10   reaction furnace was raised to 1,250°C.

By use of a pump, a raw material solution (a benzene

solution containing ferrocene in an amount of 5.5 mass% and

sulfur in an amount of 0.39 mass%) (130 g/min) and hydrogen

gas (20 L/min) were fed through the raw material feed nozzle.

15   The spray angle of the raw material solution was 60°. Under

the above conditions, reaction was allowed to proceed for one

hour to thereby produce carbon fiber. The resultant carbon

fiber was found to have a bulk density of 0.04 g/cm^3. The

carbon fiber was found to have a specific resistance of 0.03

20   Ωcm when being compressed so as to have a bulk density of

0.8 g/cm^3.

The thus-produced carbon fiber was observed under an

electron microscope, and the average diameter of fiber

filaments of the carbon fiber was found to be about 150 nm.

25   The branching degree of each fiber filament was measured and

found to be 0.13 occurrences/μm. The mass of the carbon

fiber was measured, and carbonization yield (the mass of the

produced carbon fiber/the mass of the fed benzene) was

calculated to be 60%.

Comparative Example 2:

5   The vapor grown carbon fiber produced in Comparative

Example 1 was fired at 1,000°C for 15 minutes and then

graphitized at 2,800°C for 15 minutes. The thus-graphitized

carbon fiber was dispersed in polyacetal by use of a kneader

to thereby prepare a compound. The vapor grown carbon fiber

10   was added to the resin in an amount of 5 mass%. The

resultant compound was molded into a product by use of a

thermal press, and the volume resistivity of the molded

product was measured by means of the four-terminal method and

found to be 100 Ωm.

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